INDUSTRY INTERCOMPARISON

FOR

SOLVENT EXTRACTABLES (AEG 23)

DCM vs HEXANE

Report Prepared by

Sylvia Cussion
Ontario Ministry of Environment & Energy
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SEPTEMBER 22, 1997

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BACKGROUND

In December 1996, a letter was sent to all Ontario industries that are required to monitor their effluent streams for Solvent Extractable Materials (ATG 25), requesting their participation in an intercomparison of extraction solvents. The industries were requested to collect duplicate samples for eight consecutive sampling dates during February and March of 1997. One sample was to be analyzed using the regulatory solvent, dichloromethane (DCM), and the second sample was to be analyzed using the proposed new solvent, n-Hexane (Hexane). The purpose of this study was to determine if there was a significant difference between the two solvents for as many different effluent types as possible, and determine if there may be an impact on the regulatory limits. The target date for amending the regulations is the fall of 1997, with implementation January 1998.

Several industries were unable to participate in the specified time frame. Several industries indicated that they would participate, though not all reported results. Data were received from eleven industries, representing four industrial sectors. The data was analyzed both for individual industries and grouped by sector.

STATISTICAL EVALUATION

The data, grouped by sector, was plotted on a scatter plot (Figure 1). The range between 0 - 5 ppm was expanded in Figure 2.

Data are provided in Table 1. Each industry has been assigned an ID Code to protect confidentiality. In the case of industries that provided data from more than one sampling point, the industry's internal identifier has also been changed. The results from the two solvents for each date, represent paired data. The difference was determined for each data pair. The distribution of the differences, grouped by sector, is provided in Figure 3. Distribution plots for selected industries are provided in Figures 4 - 7, and are discussed below.

Two statistical tests were applied to the data, both by sector and for individual industries. The Paired t-Test, which is appropriate for normally-distributed data, and the non-parametric Sign Test were both applied. The outcomes are provided in Table 2. The appropriateness of each test for each data set is discussed below.

DISCUSSION OF RESULTS

The scatter plots (Figures 1 and 2) do not show any specific pattern to the results. There is however, a tendency for slightly lower results when Hexane is used as the extraction solvent.

The distribution of the differences (Figure 3) varies for each sector. Both the Petroleum sector (1 industry) and Inorganic Chemical sector (3 industries) have distributions that are close to normal. The Iron & Steel sector (2 industries) have a normal distribution for the bulk of the data, with 3 outlying results forming a tail in the positive direction. The Organic Chemical sector does not have a normal distribution. There are

two modes (0 and 2-2.5 ppm), and several outlying results in both directions.

Organic Chemical Sector

When the data from the 5 industries that are part of the Organic Chemical sector are combined, the data has a bimodal distribution, as noted above. The non-parametric Sign Test (Table 2) indicated that there is a statistically significant difference between the results from the two solvents. (The Paired t-Test provided the same result.) Removing the outlying results (absolute difference between solvents of greater than 4 ppm) did not change the outcome of the Sign Test or the Paired t-Test.

Data from OC1 formed two groups, differences of 2 ppm or less for 4 sample pairs and differences of greater than 8.5 ppm for the remaining sample pairs. While the Sign Test did not indicate that there was a significant difference between the two solvents, the data set suggests that the effluent may have been different during the period Feb. 10 to Mar. 3. DCM may have extracted materials from the effluent stream during this period that were not extractable using Hexane. This suggests that there is significant difference between the two solvents that may require further investigation.

OC2 provided data from three different effluent streams. The Paired t-Test did not indicate a significant difference between the solvents for the combined data. However, when the data is examined, the results from sampling point #1 show a slight positive bias for the DCM (Figure 4 and Table 1). The Paired t-Test for this effluent stream barely indicated that there may be a statistically significant difference between the two solvents. The Sign Test for the combined data is heavily weighted by the data from sampling point #1 (data pairs with a difference of "0" are dropped from the calculation; most of the data from the other two sampling points had a difference of "0"). The Sign Test also indicated that there may be a statistically significant difference between the two solvents.

All the results from OC3 using DCM were higher than using Hexane. The Paired t-Test demonstrated a significant difference between the two solvents. The Sign Test was not applicable.

The Paired t-Test indicated no significant difference between the solvents for the results from OC4. However DCM tends to produce higher results (Figure 5), except for one data pair. The Sign Test suggests that there may be a significant difference between the two solvents.

The results from OC5 suggest a positive bias for DCM (Figure 6). The Paired t-Test indicated a statistically significant difference between the two solvents.

Inorganic Chemical Sector

The combined data from the three industries that are part of the Inorganic Chemical sector have a close to normal distribution. The Paired t-Test indicated that there was a significant difference between the two solvents. (The Sign Test provided the same results). When the industries are evaluated separately, the Paired t-Test results for IC2 and IC3 indicated no significant difference between the two solvents for the effluents from these two industries. However, the Paired t-Test result for IC1 did indicate a statistical difference between the two solvents. When the actual data from IC1 is examined (Table 1), all of the values reported from analysis by both solvents are 3 ppm or less. The reported Detection Limit is 1 ppm, so all reported results were at or near this limit. As well, these values are all well below the regulatory discharge limit of 15 ppm. From an analytical point of view, the results from IC1 do not indicate a difference between the two solvents, nor is there reason for concern from a regulatory perspective.

Iron & Steel Sector

Two industries from this sector provided data. When combined, the Paired t-Test and the Sign test indicated that there was a statistically significant difference between the two solvents (Table 2). When the two industries were evaluated separately, IS2 demonstrated no significant difference between the two solvents, while IS1 did demonstrate a significant difference. When the distribution of the differences for the Iron & Steel sector is examined, there are three outlying results (Figure 3). These points are from 3 data pairs from IS1 (Figure 7), who contributed the majority of the data for this sector (from 8 discharge points). If these 3 outlying points are removed, then the remaining IS1 results demonstrate no significant difference between the two solvents.

Petroleum Sector

Only 1 industry from the Petroleum Sector (PETRO) reported results for this study. The differences between the two solvents had a normal distribution (Figure 3). The Paired t-Test (Table 2) indicated that there was no statistically significant difference between the two solvents. (The Sign Test provided the same result.)

LSB INTERCOMPARISON

During the same period, LSB also received duplicate samples from several industries, and analyzed one sample using DCM and the other using Hexane. The results are provided in Table 3. They represent several industrial sectors, as indicated. In all cases, the difference between the two solvents was 0.5 ppm or less, with an even distribution of positive and negative differences. There is insufficient data to do any statistical analysis, but the available data does not suggest that there is a difference between the two solvents for these effluent types.

CONCLUSION

The results from this study indicate that no statistically based decision may be made that applies to all effluent types. There is a tendency for DCM to extract more material from the effluents than Hexane can. However, in most cases (93% of the data pairs), this difference is less than 3 ppm. Some individual effluent streams may require further comparisons between the two solvents. However for the majority of the effluent streams, there should be no significant change in the data by replacing DCM with Hexane as the extraction solvent for ATG 25.

TABLE 1

OC1

Date	DCM	Hexane
03–Feb–97	4.4	4.2
10–Feb–97	8.6	<1
17–Feb–97	14	1.3
24–Feb–97	17	2.4
03–Mar–97	12	1.6
10–Mar–97	3.2	1
17–Mar–97	1.9	2.1
24–Mar–97	4.2	4.9

OC2

SAMPLE #1

Date	DCM	Hexane
03–Feb–97	<1	<1
10–Feb–97	4.3	4
17–Feb–97	2.7	2.4
24–Feb–97	3.6	1.8
03–Mar–97	2.9	2.5
10–Mar–97	11	7.5
17–Mar–97	2.4	1.6
24–Mar–97	2.9	2.6

SAMPLE #2

03–Feb–97	<1	<1
10–Feb–97	<1	<1
17–Feb–97	<1	<1
24–Feb–97	<1	<1
03–Mar–97	<1	<1
10–Mar–97	<1	1.6
17–Mar–97	<1	<1
24–Mar–97	<1	<1

SAMPLE #3

	DCM (On site)	Hexane (Private lab)
11–Feb–97	0.4 <dl	<1.0
18–Feb–97	0.2 <dl	<1.0
25–Feb–97	2.0	2.0
04–Mar–97	0.6 <dl	<1.0
11–Mar–97	0.2 <dl	<1.0
18–Mar–97	0.2 <dl	<1.0
25–Mar–97	1.6	<1.0
01–Apr–97	1.4	1.0

OC3

Date	DCM	Hexane
11–Feb–97	2	0.45
18–Feb–97	6.9	0.49
25–Feb–97	2.1	<.2
25–Mar–97	2.4	0.33
01–Apr–97	1.7	0.34
08–Apr–97	1.8	1.2
15–Apr–97	2.5	1.2
22–Apr–97	2.2	0.64

OC4

Date	DCM	Hexane
04–Feb–97	4.8	2.9
11–Feb–97	5.8	1.3
18–Feb–97	3.5	0.8
25–Feb–97	3.71	1.55
04–Mar–97	9.9	14.6
11–Mar–97	0.6	0.4
18–Mar–97	1.91	0.79
25–Mar–97	4.3	2

OC5

Date	DCM	Sample Vol	Hexane	Sample Vol
04–Feb–97	2.33	1330	0.46	1300
07–Feb–97	6.16	1380	4.77	1370
11–Feb–97	2.76	760	N/A	–
14–Feb–97	1.65	1550	2.07	1580
18–Feb–97	<1	1500	<1	1500
21–Feb–97	<1	1480	<1	1490
25–Feb–97	4.34	1450	<1	1500
28–Feb–97	1.22	1560	0.62	1620
04–Mar–97	2.34	1570	N/A	1580
07–Mar–97	4.42	1680	2.15	1670
11–Mar–97	2.33	1630	0.87	1650
14–Mar–97	1.3	1460	2.11	1470
18–Mar–97	<1	1460	0.35	1510
21–Mar–97	2.01	1490	0.37	1500
25–Mar–97	4.5	1290	4.4	1290
28–Mar–97	1.77	1580	<1	1570

TABLE 1 Continued

IS1

SAMPLE #1			SAMPLE #5		
Date	DCM	Hexane	Date	DCM	Hexane
10-Feb-97	1.1	1.6	10-Feb-97	0.4	1.5
17-Feb-97	1.3	n/a	17-Feb-97	0.9	1
24-Feb-97	1.7	1.1	24-Feb-97	0.6	0.3
03-Mar-97	6.3	1.1	03-Mar-97	0	0.7
10-Mar-97	0.5	0	10-Mar-97	0.5	0
17-Mar-97	0.3	0.5	17-Mar-97	0.4	0.4
24-Mar-97	0	1.7	24-Mar-97	0.9	0
31-Mar-97	1.1	0.6	31-Mar-97	0.4	0
SAMPLE #2			SAMPLE #6		
10-Feb-97	0	1.1	10-Feb-97	2.2	1.3
17-Feb-97	0.5	1.1	17-Feb-97	0	0.6
24-Feb-97	0.4	0.3	24-Feb-97	0.7	0.5
03-Mar-97	0.8	0.4	03-Mar-97	0	0.9
10-Mar-97	0	0	10-Mar-97	0.7	0
17-Mar-97	0.8	0.3	17-Mar-97	0.6	0.6
24-Mar-97	2.3	1.8	24-Mar-97	1.3	1.1
31-Mar-97	1.5	1.2	31-Mar-97	0.9	0
SAMPLE #3			SAMPLE #7		
10-Feb-97	0.4	0.7	10-Feb-97	0.9	1.3
17-Feb-97	0	0.6	17-Feb-97	0.2	0
24-Feb-97	0.6	0.5	24-Feb-97	0.4	0.3
03-Mar-97	0	0.6	03-Mar-97	0.3	0.6
10-Mar-97	0.7	0.4	10-Mar-97	0.2	0
17-Mar-97	5.2	0.3	17-Mar-97	0.4	0
24-Mar-97	0.3	0.5	24-Mar-97	0.4	0.3
31-Mar-97	0.6	0.2	31-Mar-97	2.4	1.9
SAMPLE #4			SAMPLE #8		
10-Feb-97	0.6	0.7	10-Feb-97	2.1	1.5
17-Feb-97	0.2	0.7	17-Feb-97	0.7	0.8
24-Feb-97	0.9	0.9	24-Feb-97	6.6	1
03-Mar-97	0.4	0.3	03-Mar-97	0.3	1.1
10-Mar-97	0	0	10-Mar-97	2.4	0
17-Mar-97	1.3	0	17-Mar-97	1.6	0
24-Mar-97	0.6	0.8	24-Mar-97	0.2	0.8
31-Mar-97	0.5	0	31-Mar-97	1.7	0.2

IS2

Date	DCM	Hexane
06-Feb-97	2.8	1.8
13-Feb-97	3.3	3.8
20-Feb-97	3.9	3.3
27-Feb-97	2	2
06-Mar-97	1.5	2.1
13-Mar-97	3	2.9
20-Mar-97	2.8	1.8
27-Mar-97	4.2	3.8

TABLE 1 Continued

IC1

SAMPLE #1

Date	DCM	Hexane
06-Feb-97	2	<1
12-Feb-97	2	1
19-Feb-97	2	1
26-Feb-97	<1	<1
05-Mar-97	1	1
12-Mar-97	1	1
19-Mar-97	2	1
26-Mar-97	1	<1

SAMPLE #2

06-Feb-97	3	1
12-Feb-97	2	1
19-Feb-97	2	2
26-Feb-97	1	1
05-Mar-97	2	1
12-Mar-97	2	1
19-Mar-97	1	1
26-Mar-97	<1	1

IC2

Date	DCM	Hexane
04-Feb-97	30.8	28.9
10-Feb-97	1.5	1.5
17-Feb-97	0.9	0.7
24-Feb-97	1.6	1.9
03-Mar-97	3.2	3.1
10-Mar-97	0.2	0.1
17-Mar-97	1.4	2.1
24-Mar-97	0.4	0.1
31-Mar-97	21.1	22.1

IC3

Date	DCM	Hexane
05-Feb-97	<.2	<.2
12-Feb-97	1	<.2
19-Feb-97	2.5	<.2
26-Feb-97	0.87	<.2
05-Mar-97	0.61	0.46
12-Mar-97	1.2	<.2
19-Mar-97	1.577	2.812
26-Mar-97	2.177	1.775

PETRO

Bioeffluent

Date	DCM	Hexane
04-Feb-97	0.3	0.2
11-Feb-97	1.6	1.8
18-Feb-97	0.8	2.5
25-Feb-97	1.6	3.8
04-Mar-97	0.6	0.3
11-Mar-97	0.4	0.6
18-Mar-97	1.1	0
25-Mar-97	0.5	0.1

Bioeffluent – Replicate

	DCM	Hexane
04-Feb-97	0.2	0.3
11-Feb-97	0.9	1.5
18-Feb-97	0.7	
25-Feb-97	1.4	3
04-Mar-97	0.8	0.4
11-Mar-97	0.3	1.1
18-Mar-97	0.3	0
25-Mar-97	0.7	0

TABLE 2 - STATISTICAL EVALUATION

SECTOR/INDUSTRY	PAIRED OBSERVATIONS	SIGN TEST
ORGANIC CHEMICAL (ALL)	Sig. Diff	Sig. Diff
OC1	Sig. Diff	no sig. diff
OC2	no sig. diff	Sig. Diff
OC3	Sig. Diff	N/A *
OC4	no sig. diff	Sig. Diff
OC5	Sig. Diff	no sig. diff
INORGANIC CHEMICAL (ALL)	Sig. diff	Sig. Diff
IC1	Sig. Diff	Sig. Diff
IC2	no sig. diff	no sig. diff
IC3	no sig. diff	no sig. diff
IRON & STEEL (ALL)	Sig. Diff	Sig. Diff
IS2	no sig. diff	no sig. diff
IS1 (all data) IS1 (3 outliers removed)	Sig. Diff no sig. diff.	Sig. Diff no sig. diff.
PETROLEUM (PETRO)	no sig. diff	no sig. diff

* Sign Test not applicable, as all DCM results were greater than Hexane results

TABLE 3 - LSB INTERCOMPARISON

Sample Date	Sample #	DCM (ppb)	Hexane (ppb)	Industrial Sector
17-Feb-97	C40350-0001	0.5 <W	0.4 <T	Iron & Steel
17-Feb-97	C40350-0002	0.5 <W	0.4 <T	Iron & Steel
25-Feb-97	C40566-0001	0.5 <W	0.4 <T	Inorganic Chemical
25-Feb-97	C40566-0003	0.5 <W	0.4 <T	Inorganic Chemical
4-Mar-97	C40743-0001	2.0 <T	1.5	Organic Chemical
10-Mar-97	C40963-0001	1.0 <T	0.8 <T	Inorganic Chemical
10-Mar-97	C40964-0002	1.0 <T	0.8 <T	Inorganic Chemical

FIGURE 1

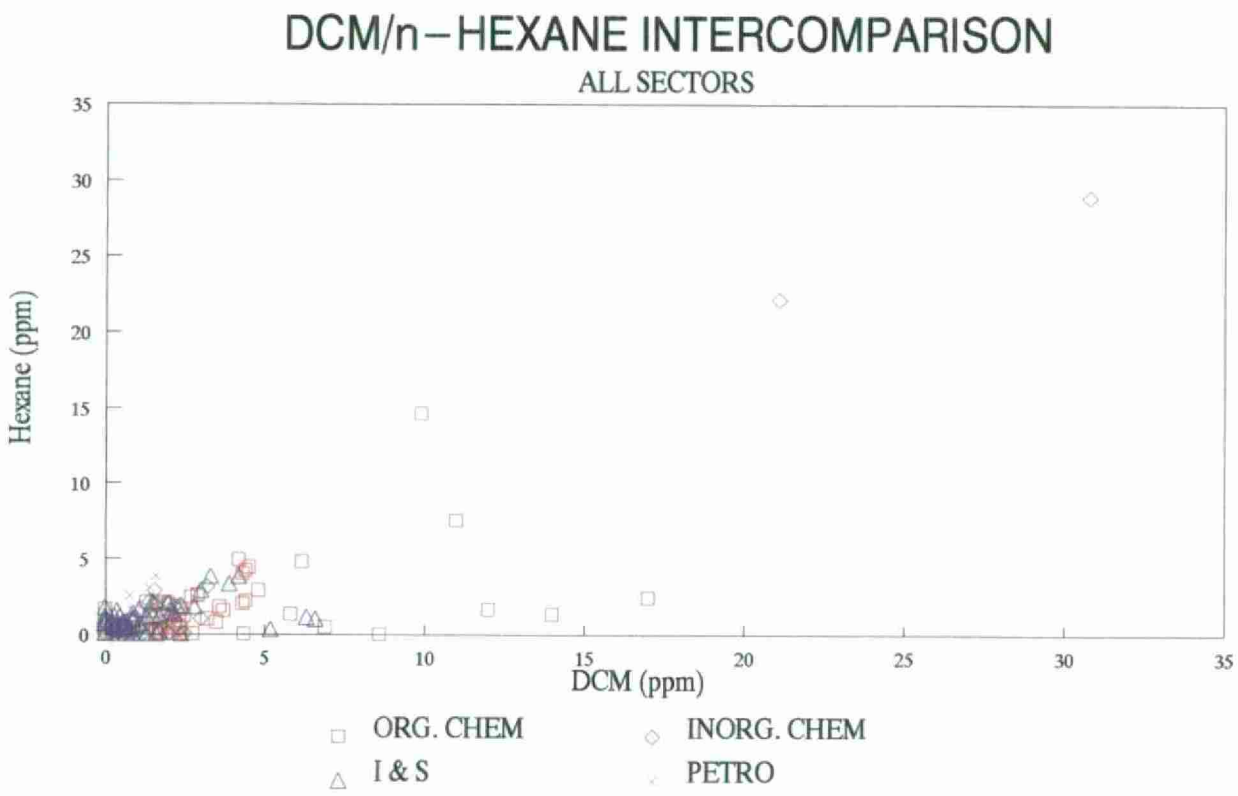

FIGURE 2

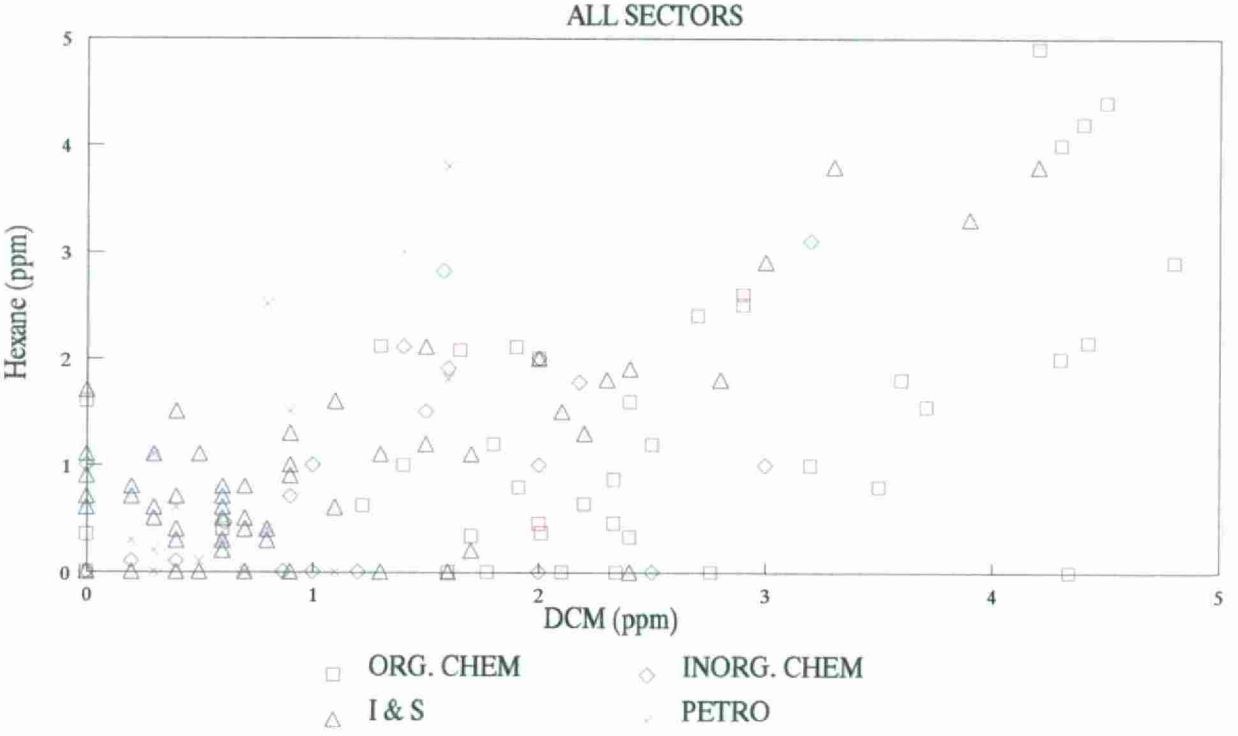

FIGURE 3

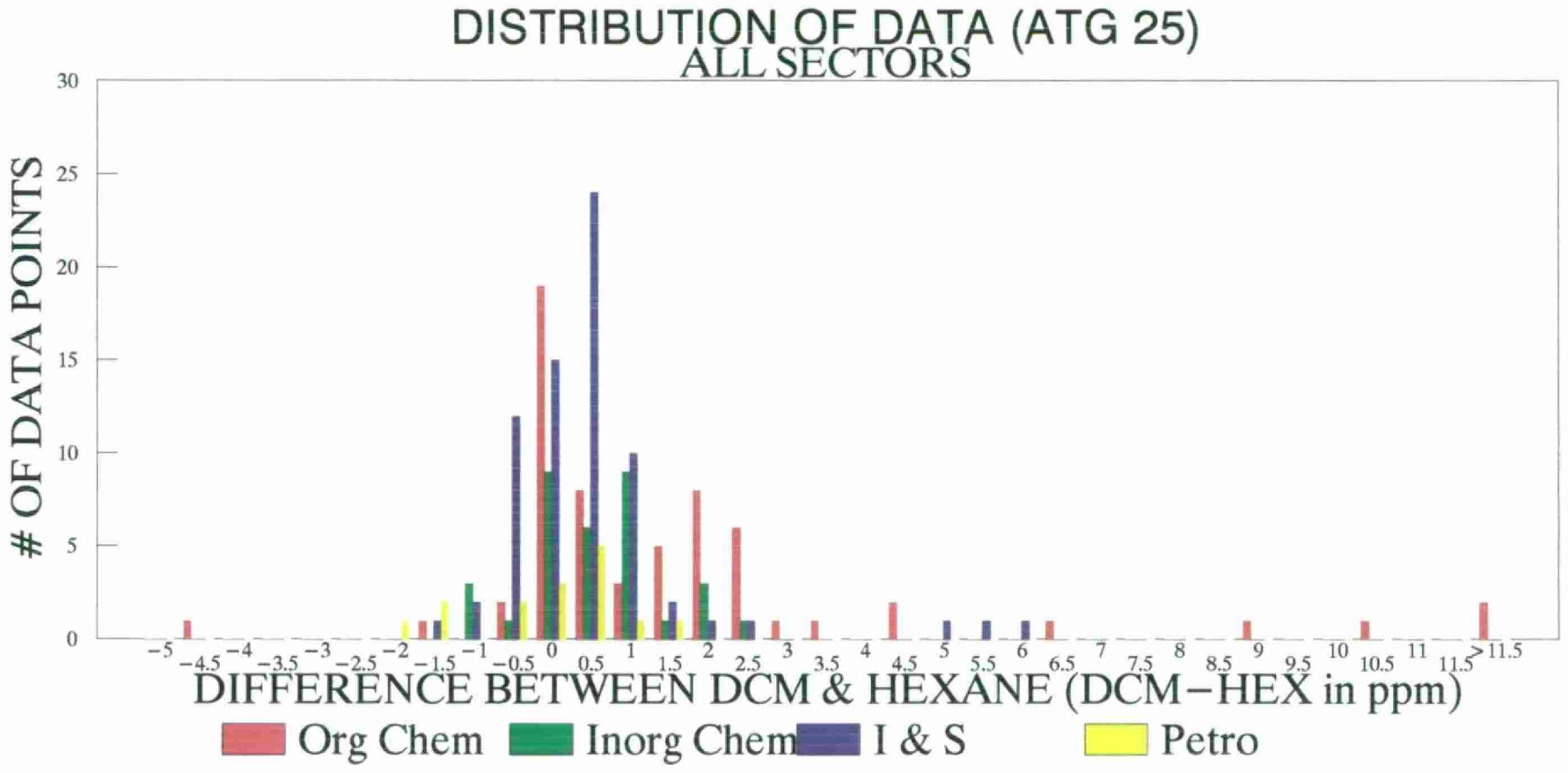
DISTRIBUTION OF DATA (ATG 25)
ALL SECTORS
OF DATA POINTS
30
25
20
15
10
5
0
−5 −4.5 −4 −3.5 −3 −2.5 −2 −1.5 −1 −0.5 0 0.5 1 1.5 2 2.5 3 3.5 4 4.5 5 5.5 6 6.5 7 7.5 8 8.5 9 9.5 10 10.5 11 11.5 >11.5
DIFFERENCE BETWEEN DCM & HEXANE (DCM−HEX in ppm)
Org Chem
Inorg Chem
I & S
Petro

FIGURE 4

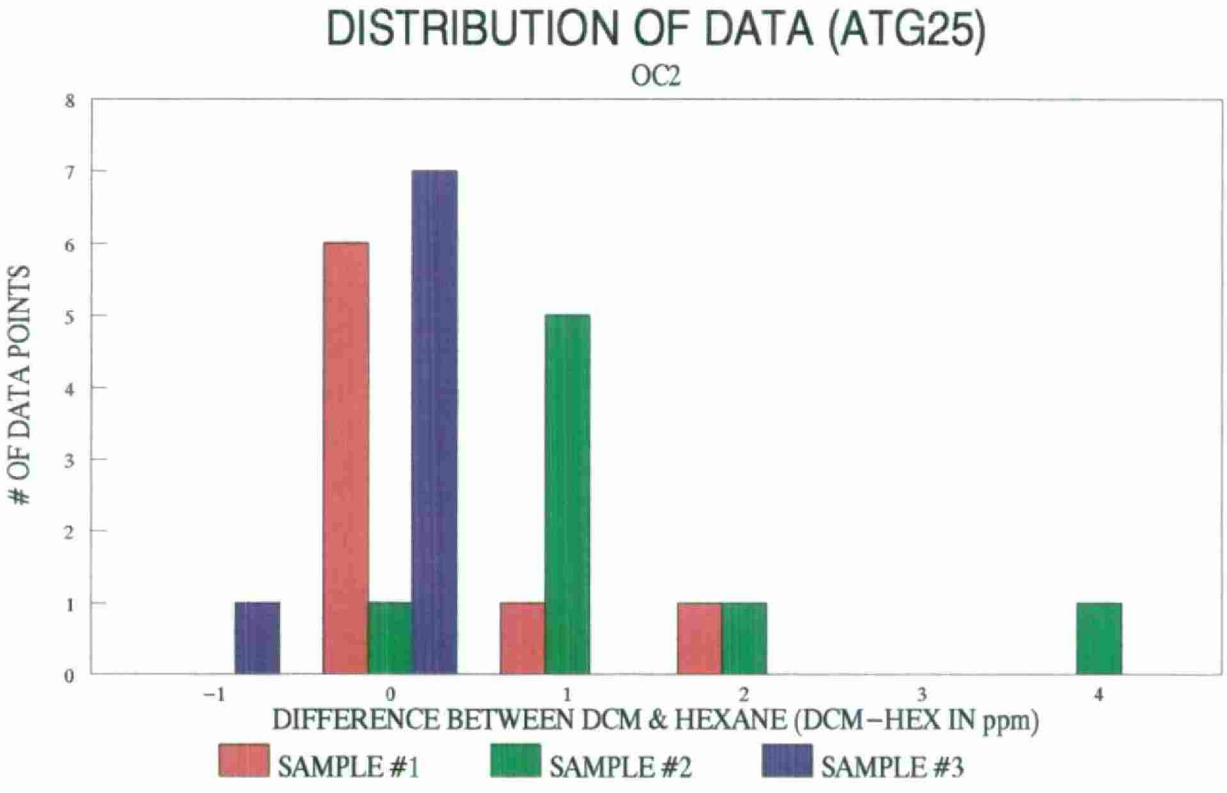

FIGURE 5

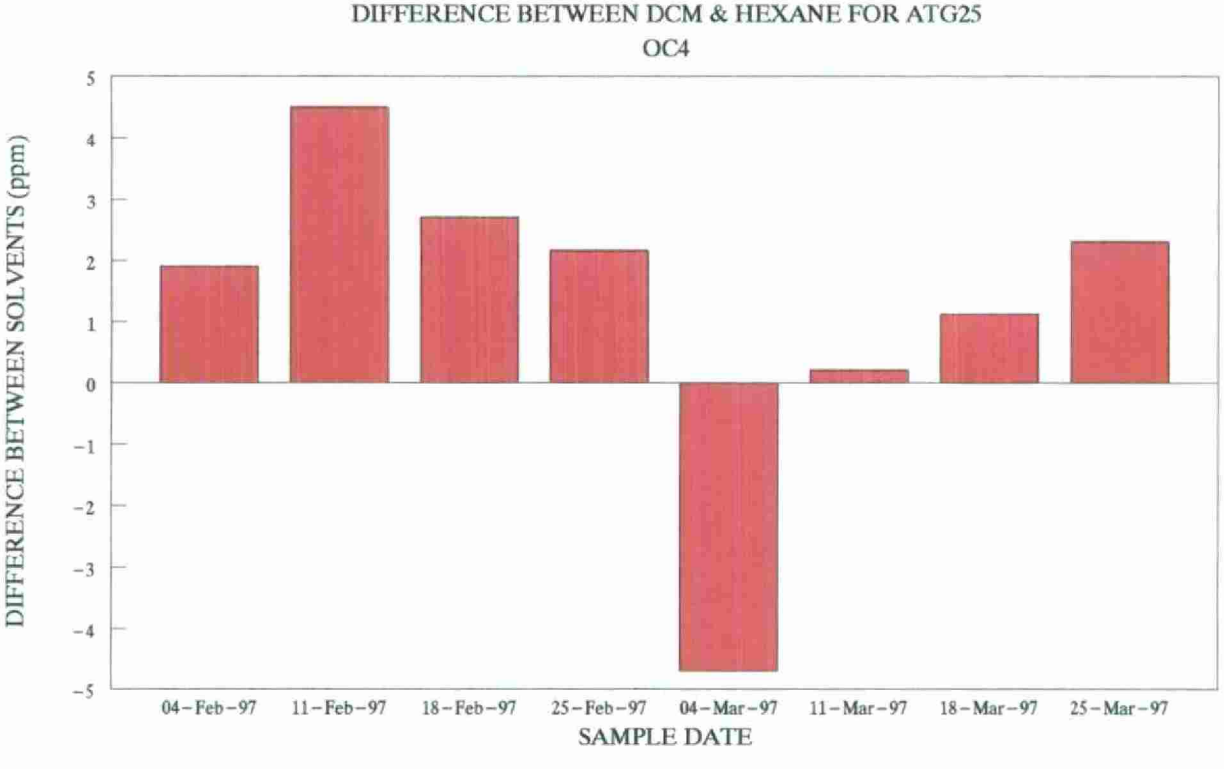

FIGURE 6

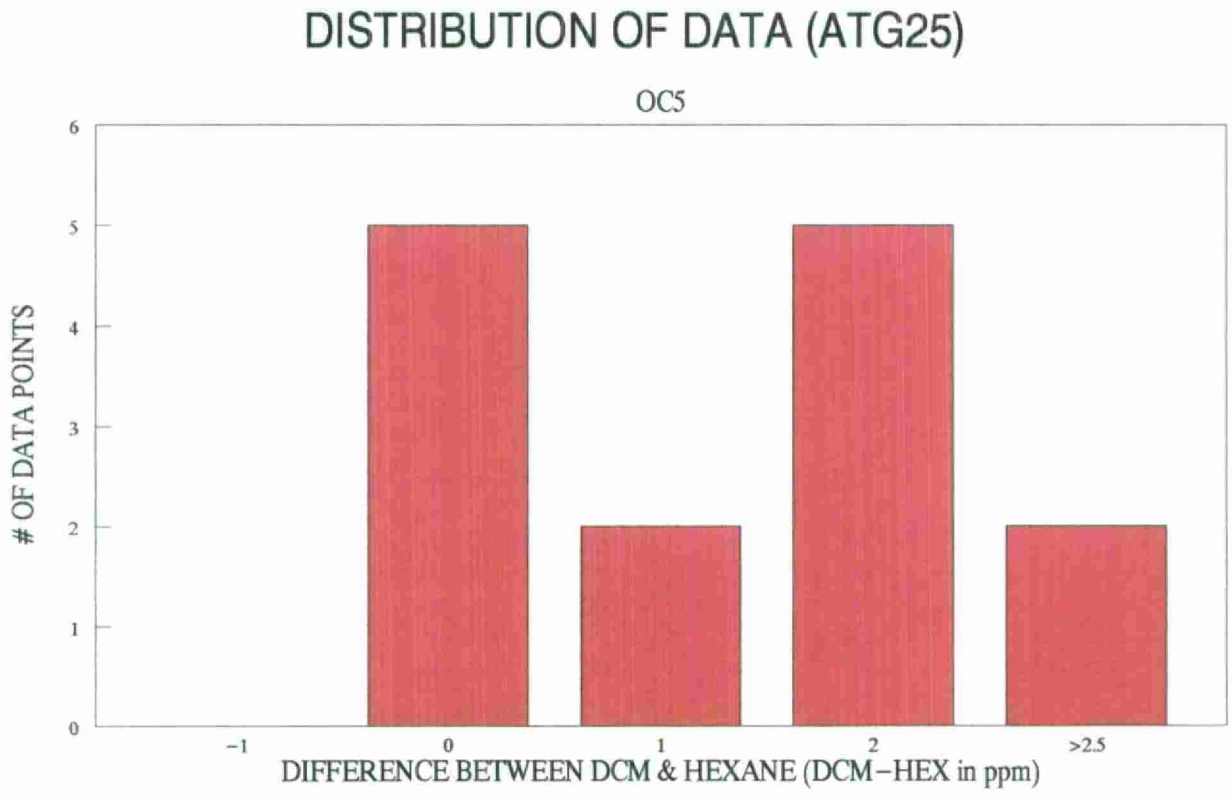

FIGURE 7